

PATENT SPECIFICATION

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- (72) Inventor JOHN GEORGE GIBSON



(54) IMPROVEMENTS RELATING TO ALKALI METAL-SULPHUR CELLS

(71) We, CHLORIDE SILENT POWER LIMITED, a Company incorporated under the laws of Great Britain, of 52 Grosvenor Gardens, London, S.W.1, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to alkali metal-sulphur cells, e.g. sodium-sulphur cells, in which the electro-chemical reactants are, at the operating temperature of the cell, molten alkali metal as negative active material (anodic material) and molten sulphur material as positive active material (cathodic material) and anode and cathode compartments are separated by a solid electrolyte, e.g. beta-alumina in the case of sodium-sulphur cells.

15 The object of this invention is to provide an improved form of cathode, i.e. sulphur electrode.

20 The form of sulphur electrode which has been most investigated so far in connection with molten alkali metal-sulphur secondary cells consists of a three-dimensional electronically conducting matrix compressed between the surfaces of an electronically conductive pole (i.e. a current collecting pole) and the solid electrolyte and impregnated with the positive active material (molten sulphur, sodium polysulphides). A typical sulphur electrode consists of compressed 25 graphite felt impregnated with sulphur. In the case of tube cells having an inner tubular member formed by the electrolyte and a metal outer tubular member, such a sulphur electrode may be contained within the electrolyte tube and an electronically conductive current collecting pole then extends down into the tubular electrolyte member through the electronically conductive matrix. Alternatively the sulphur electrode may be 30 contained in the annular space between the two tubular members, in which case the outer tubular member constitutes the electronically

35 conductive pole associated with the sulphur electrode.

40 It is a fundamental property of such a three-dimensional system that the reaction rate is non-uniform during charge and discharge. This means that when discharging to a nominal overall composition Na_2S_3 it is possible for lower, insoluble sulphides e.g. Na_2S_2 and Na_2S , to form in some regions of the electrode whilst other regions are still at compositions more sulphur-rich than Na_2S_3 . Also, when charging, it is possible to cause premature polarisation by forming a layer of sulphur on the surface of the beta-alumina. This layer of sulphur can effectively isolate the remainder of the electrode and prevent its further charging.

45 In order to mitigate against these conditions, in accordance with the invention, a sulphur electrode of an alkali metal-sulphur cell comprises an electronically conducting pole in the form of an inflexible body and the sulphur material which extends between and is in contact with said pole and the adjacent surface of the solid electrolyte, the surface of the pole in contact with the sulphur material having a grooved configuration, whereby the surface area of said pole surface is greater than the surface area of the electrolyte in contact with the sulphur material.

50 The design of sulphur electrode in accordance with the invention can best be derived assuming the following two conditions, namely:

1. that the whole of the electrochemical reaction (charge or discharge) can take place at the surface of the electronically conductive pole at a rate corresponding to, about 40 mA/cm^2 .
2. that the normal operating rate of a sodium/sulphur cell corresponds to about 150 mA/cm^2 referred to the electrolyte surface area.

55 The invention will now be further explained with reference to the accompanying diagrammatic drawings, in which:

60 Figure 1 is an explanatory diagram,

65 70 75 80 85 90 95

Figure 2 shows two sulphur electrodes embodying the invention, and

Figure 3 shows a further embodiment.

Consider, by way of example, the situation illustrated in Figure 1 of the accompanying drawings. This shows in sectional elevation the cathode compartment of a sodium sulphur cell defined by the interior of beta-alumina tube 3 constituting the solid electrolyte of the cell. To complete the cell the tube 3 would be surrounded by an outer tubular member, the annular space thus provided between the two tubular compartments constituting the anode compartment of the cell.

A cylindrical electronically conductive pole 1 is immersed in a pool 2 of molten cathodic material, i.e. sulphur, contained in the tube 3. The radius of the pole 1 is r (mm) and that of the beta-alumina tube 3 is R (mm). If the current density referred to the cylindrical surface of the beta-alumina tube 3 is 150 mA/cm^2 and that referred to the cylindrical surface of the pole 1 is 40 mA/cm^2 then

$$\frac{R}{N \times r} = 40 \quad (1)$$

Where N , the enhancement of the surface area, can be likened to a surface roughness factor.

In a particular case, for example $R=16 \text{ mm}$ and $r=8 \text{ mm}$, equation (1) gives a value of 7.5 for N . Such an increase in the apparent geometrical surface area of the pole can be achieved in several ways.

Two possibilities for increasing the apparent surface area of the pole by giving it a grooved configuration are illustrated in the composite Figure 2 of the accompanying drawings. Both these examples can be realised in practice by normal screw-cutting methods starting from a plain cylindrical pole member. In both cases the formulae for calculating the helical thread dimensions hold true provided the depth of the thread is small compared to the radius of the pole. Thus in the case of the saw-tooth form shown on the left-hand side of Figure 2 it is given by

$$\theta = \sin^{-1}\left(\frac{1}{N}\right)$$

where θ is the angle shown and in the case of the square wave form shown on the right-hand side of Figure 2 it is given by

$d=(N-1)h$ where d and h are the dimensions shown.

Such an enhancement of the surface area can be produced in a variety of other ways. Thus, rather than machining a true thread

the desired increase in surface area could be produced by a series of adjacent parallel-sided rings defining between them a series of circumferential grooves as shown in Figure 3, or milled or extruded as a series of grooves parallel to the major axis of the cylinder.

A pole with such an enhanced surface area can be made from a variety of electronically conducting materials including carbon (and various graphites) stainless steel and other corrosion resistant metals and alloys and mild steel and other alloys which are subsequently given a corrosion proofing treatment.

Furthermore the above principles apply to a sulphur electrode constructed in the reverse manner, i.e. with the sulphur electrode surrounding the beta-alumina tube 3. In this case the sulphur electrode consists of a reservoir of sulphur contained inside a tubular pole. The interior of the tube 3 would then constitute the anode compartment of the cell and so contain alkali metal. Considering again the example given with reference to Figure 1, but whereas in this case $R=8 \text{ mm}$ and $r=16 \text{ mm}$, the enhancement factor N is equal to about 1.9. This can be obtained, as before, by suitable machining of the inner surface of the cylindrical pole.

Similarly the idea may be extended to planer cells where the pole, in the form of a flat plate, may, for instance, have a groove of appropriate dimensions cut as a spiral on its surface facing the electrolyte which would be in the form of a plate. It is necessary to provide some means of starting the electrode, because sulphur is an insulator. A suitable starting device would consist of a thin ring of carbon felt or compressed carbon sheet forming an electronic contact between the pole and the surface of the beta-alumina. The sole purpose of this is to allow the first discharge cycle to commence in order to generate some ionically conducting reduced species. The preferred location for the starter would be near the top of the pole just below the surface of the sulphur because, then, gravity would accelerate the mixing of the reduction products, which are more dense than pure sulphur. A typical design for a working sulphur electrode is shown, as an example, in Figure 3, where the starting device is indicated at 4.

WHAT WE CLAIM IS:—

- An alkali metal-sulphur cell in which the electro-chemical reactants are, at the operating temperature of the cell, molten alkali metal as negative active material and molten sulphur material as positive active material and anode and cathode compartments are separated by a solid electrolyte, wherein a sulphur electrode comprises an electronically conducting pole in the form of

- an inflexible body and the sulphur material which extends between and is in contact with said pole and the adjacent surface of the solid electrolyte, the surface of the pole in contact with the sulphur material having a grooved configuration whereby the surface area of said pole surface is greater than the surface area of the solid electrolyte in contact with the sulphur material.
2. An alkali metal sulphur cell according to claim 1, wherein said surface area of said pole is greater than said surface area of the solid electrolyte by an amount such that the ratio of the current density at said pole surface to the current density at said electrolyte surface is about 4:15.
3. An alkali metal-sulphur cell according to claim 1 or 2, wherein said pole body is of cylindrical form and extends into said sulphur material which is contained within a tubular solid electrolyte, the cylindrical surface of said pole body having a circumferentially ex-
- tending groove or grooves to provide said grooved configuration.
4. An alkali metal-sulphur cell according to claim 3, wherein said pole body is provided with a helically extending groove.
5. An alkali metal-sulphur cell according to claim 1 or 2, wherein said pole body is of tubular form and surrounds said solid electrolyte which is also of tubular form, the sulphur material being contained within said tubular pole body.
6. An alkali metal sulphur cell having a sulphur electrode substantially as described with reference to and as shown in Figure 2 or Figure 3 of the accompanying drawings.

JENSEN & SON,
Agents for the Applicants,
8 Fulwood Place,
London, WC1V 6HG.
Chartered Patent Agents.

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Fig. 1

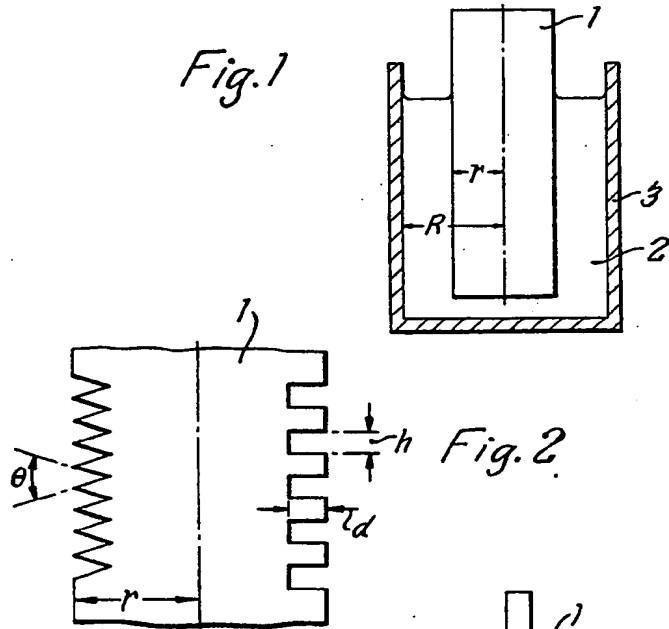


Fig. 2

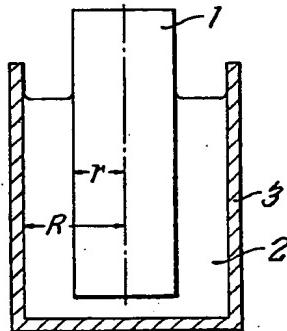


Fig. 3

